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e.m.f. and impedance of Na–S cells and sodium polysulphides during freeze–thaw cycles

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The dependence of the e.m.f. and the resistance of Na–S cells on temperature was determined in order to understand the processes occuring during freezing and thawing of the positive electrode. It turned out that there is a strong tendency for the sodium polysulphides even in graphite felt to undercool and to crystallize only at a very slow rate in the frozen state. At the freezing point e.m.f. and impedance show discontinuities which could be interpreted using the phase diagram. The freeze–thaw behaviour of Na_2S_3 is different from that of the other compositions concerning its conductivity, diffusion properties and adhesion to the wall of the casing. These findings are useful for the analysis of failures due to thermal cycling.

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1. Introduction

The sodium–sulphur battery (Beta battery) is being developed for electric vehicle propulsion and offpeak energy storage [1]. The anode consists of sodum, the cathode of a sodium polysulphide Na_2S_x with x from 3 to about 20. A β-Al_2O_3 tube is used as separator. At the operating temperature of about 330° C the polysulphides are liquid according to the phase diagram as shown in Fig. 1. In the two-phase region two melts exist and the e.m.f. is accordingly a constant 2.076 V at 330° C. When cooled down, Na_2S_5 solidifies whereas sulphur remains liquid until 119° C is reached. In the one-phase region, where the e.m.f. drops from 2.076 to 1.78 V there are two eutectics and solidification is complete at 235° C. However, it is well known, that the melt shows a strong tendency to undercool, expecially in the one-phase region [2, 3]. In addition, amorphous states were observed and it seems that the solidification characteristic of sodium polysulphide is governed by rather non-predictable nucleation processes.

A sodium–sulphur battery in a vehicle should be able to cool down to room temperature from time to time. Therefore it is necessary to investigate the processes occurring during freeze–thaw cycles. This is described in the following by looking predominantly at the change in the e.m.f. and the resistance of complete cells. In addition, measurements were carried out also in electrochemical half-cells without graphite felt.

2. Experimental details

Thermal cycling was performed with BBC standard cells (50 A h theoretical capacity) at different states of discharge. The cells were cooled and heated with a constant rate, usually 25° C h^{-1}. Two types of furnace were used. With the quasi-adiabatic furnace the cell-temperature during solidification was allowed to rise independent of the controlled furnace. In the isothermal furnace (calorimeter) the temperature was made to change with a constant rate also during solidification by reducing the heating power of the furnace. The heat of fusion was then determined by measuring the heating power of the furnace (for details of the arrangement see [4]). With both types of arrangement the same behaviour of e.m.f. and resistance were observed.

It turned out that, due to the high resistance of polysulphide in the solid state, the e.m.f. must be measured with a high-impedence voltmeter (10^{12} Ω input resistance). If a regular voltmeter with 10^7 Ω is used, the open circuit voltage near room temperature drops to values below 1 V. The a.c. cell resistance was determined using a Solartron

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1170 frequency response analyser. The amplitude of the signal was kept below RT/F in order to remain in the linear region of the current voltage relationship (R: gas constant, T: Temperature, F: Faraday constant).

In addition to the measurements on complete Na–S cells, the temperature dependence of the resistance of polysulphides (without graphite felt) was also determined in evacuated glass cells which contained only the polysulphide and two electrodes. The Na_2S_x for this purpose was prepared by mixing sulphur and Na_2S in the respective proportion and reacting them at 450° C [5]. The electrodes were molybdenum wires of about 1 mm diameter with a distance of about 5 mm between them. During the relative short measuring time the glass was not attacked by the polysulphides. The same results as with these cells were obtained in metal cells which were designed for corrosion experiments and in which very pure polysulphide was prepared electrochemically *in situ* [6]. The experimental difference between these polysulphide arrangements and the complete cell is that in the former the Na_2S_x was shrinking onto the measuring electrodes during freezing, thus giving good contact, whereas in a complete cell the Na_2S_x would be detached from the casing. The reason for this behaviour is the large thermal expansion coefficient of Na_2S_x of about 35 x 10^{-6} K^{-1} [7], which is higher than that of the steel casing. Therefore, different results can be expected for the resistance in the frozen state depending on the arrangement.

3. Results

During cooling, the temperature of solidification showed random values between 170 and 285° C. This is shown for one composition, namely Na_2S_4, in Fig. 2. As can be seen, the freezing temperature as well as the peak power was different for every cycle. However, the heat of fusion, which can be calculated from the integral below a peak, was the same in all cases (about 5 Wh, corresponding to literature values [3] for Na_2S_4). In the case of Na_2S_3 smaller vlaues than expected were observed, indicating partially amorphous solidification. With all compositions, undercooling occurred up to 100° C below the phase diagram value. During the thaw-cycle, however, melting was observed always at temperatures corresponding to the phase diagram, Fig. 1.

The temperature dependence of the e.m.f. of a Na–S cell at 8 different states of discharge,

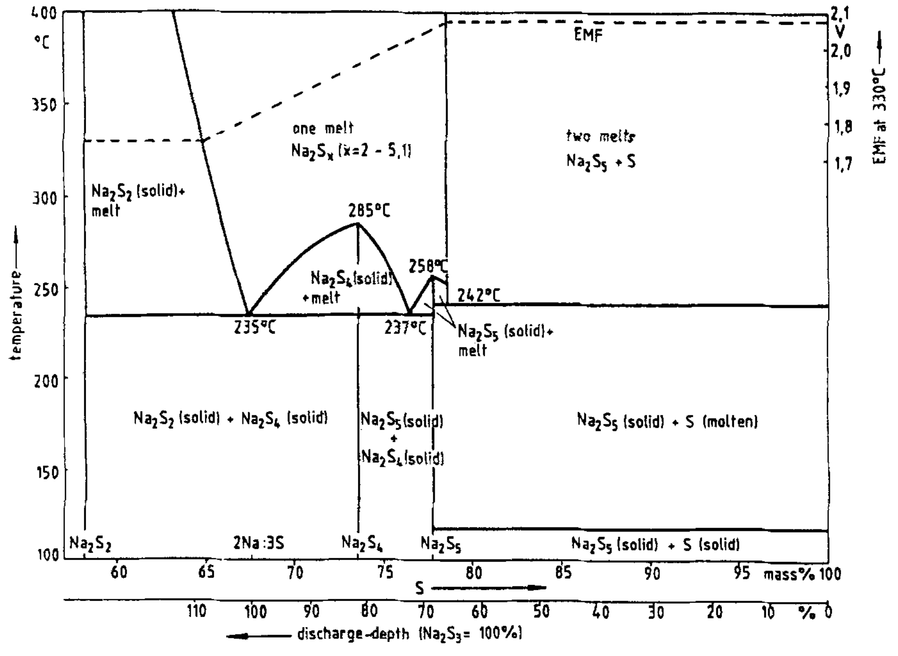

Fig. 1. Phase diagram for sulphur Na_2S_2.

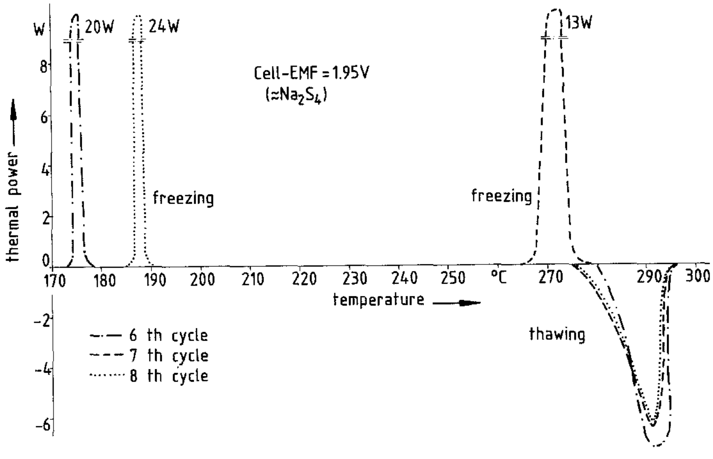

Fig. 2. Thermal power output of a partly discharged Na–S cell due to freezing and thawing, as measured in a calorimeter for thermal cycle No. 6, 7 and 8. Cooling–heating rate: 10° C h^{-1}.

corresponding to different compositions of the sodium polysulphides, is shown in Fig. 3. It can be seen, that at the solidification point the e.m.f. changed its value suddenly.

This corresponds to the relatively fast transition from the molten to the solid state as was observed especially with the undercooled melts. The e.m.f. change of Na_2S_x is positive if $x \geqslant 4$ and negative if $x \leqslant 4$. Below the solidification point only two distinct e.m.f. values were observed (within the scattering due to different crystallization kinetics), in contrast to the behaviour in the molten state, where the e.m.f. varied according to the composition [2]. Thus, by measuring the e.m.f. of a cold cell (by $a > 10^{12}$ Ω voltmeter), it can only be decided whether a cell is discharged beyond Na_2S_4 or not. It should be stressed here, that the voltage changes in Fig. 3 are real thermodynamic effects and are not correlated with a failure whatsoever. The cells function properly after repeated thermal cycling with e.m.f. changes as described. During heating up the e.m.f. increased not stepwise but slowly, as is shown in Fig. 3 for one example. Melting, as can be seen from the calorimetric measurements, occurred at a temperature between 235 and 285° C, according to the phase diagram (Fig. 1).

The a.c. resistance of Na–S cells during thermal cylcing is shown in Fig. 4 for two different states of discharge. It can be seen that in the solid state the cell which was discharged until Na_2S_4 had a resistance of about an order of magnitude higher than that discharged until Na_2S_3. In the molten state these differences are not visible because the β-Al_2O_3 tube takes most of the cell resistance. Due to the strong tendency to undercool, a hysteresis was observed with both compositions; this was more pronounced, however, in the case of Na_2S_4

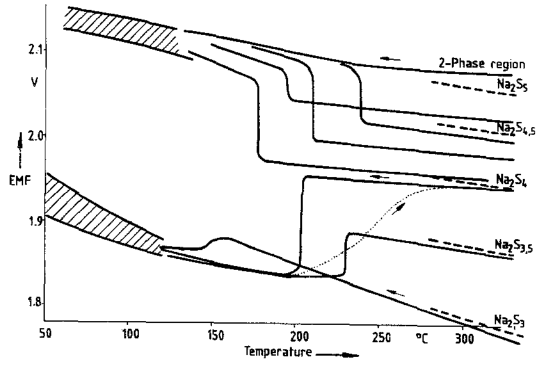

Fig. 3. e.m.f. of a Na–S cell versus temperature at different states of discharge during cooling and heating up (dotted line as one example).

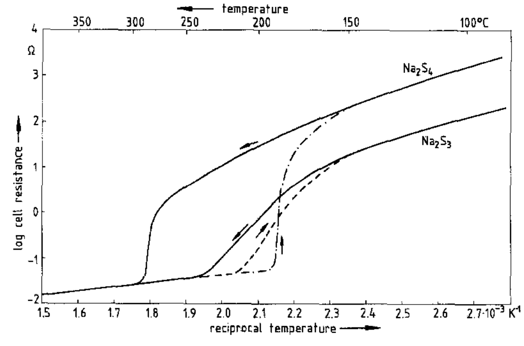

Fig. 4. Dependence of the resistance of a Na–S cell on temperature for two states of discharge, corresponding to compositions of Na_2S_3 and Na_2S_4. Measuring frequency: 30 Hz.

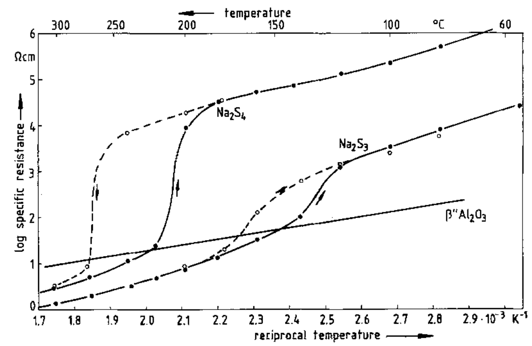

Fig. 5. Dependence of the resistance of Na_2S_3 and Na_2S_4 in glass tubes (without graphite felt) on temperature. Measuring frequency: 30 Hz.

because of the higher melting temperature. A similar behaviour can be seen from the measurements of the specific resistance of sodiumpolysulphides in glass tubes. Fig. 5 shows that the hysteresis is essentially the same as with complete Na–S cells. Differences are due to the random distribution of temperature at which solidification starts.

At high temperatures (molten Na_2S_x) the values are in good agreement with [8]. The calculation of activation energies of molten Na_2S_x is difficult because the lines are not straight. At low temperatures the activation energy for both solid Na_2S_3 and solid Na_2S_4 can be taken from Fig. 5 to be between 40 and 50 kJ mol^{-1}. For comparison, the curve for β-Al_2O_3 is also included in the figure (activation energy about 25 kJ mol^{-1}).

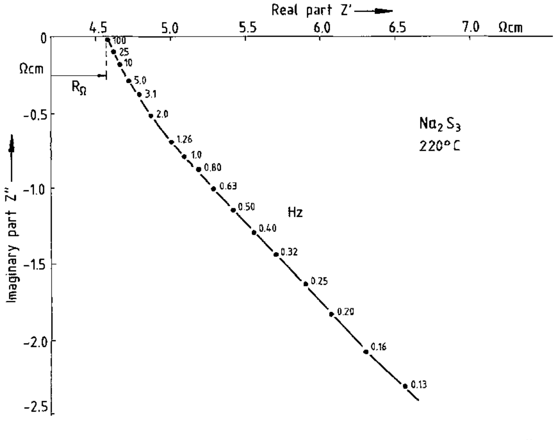

Fig. 6. Frequency dependence of the impedance of Na_2S_3 in a glass tube (without graphite felt) at 220° C (molten state).

Table 1. Activation energies for the electric resistance in kJ mol^{-1}

	cell	Na_2S_x	β-Al_2O_3
molten	18 ± 2	about 35	–
solid	48 ± 5	46 ± 5	25 ± 1

Table 1 shows the activation energies which were determined from Figs. 4 and 5.

At the melting point of the two polysulphides the resistance of β-Al_2O_3 and Na_2S_x are comparable, whereas at higher temperatures β-Al_2O_3 becomes more and more dominant as the cell resistance is concerned. The difference between Na_2S_3 and Na_2S_4 in the solid state amounts to almost two decades and therefore is more pronounced than in the complete Na–S cell (see Fig. 4). This may be due to the different kind of electrical contact with the current collector (see the discussion section).

For the measurement of the a.c. resistance, as described above, a frequency of 30 Hz was taken. Fig. 6 shows that at this frequency the impedance was almost completely ohmic which means that the electrolyte resistance without polarization was measured. For solid Na_2S_x no frequency dependence as in Fig. 6 could be obtained because the ohmic resistance became so large in comparison to the polarization resistance, that the phase angle remained below the measuring limit of about 1°.

The curves in Figs. 4 and 5 are stable with time only in the molten state region. When thermally cycled with a rate of 25° C h^{-1} between 60 and 330° C the curves were reproducible. However, after letting a cell or a glass tube with polysulphide stand for a week or two at room temperature, the resistance at 30 Hz rose during this time by several orders of magnitude, from about 10^5 to $\geq 10^8$ Ω cm for Na_2S_3. Detailed measurements on this long-term behaviour were not carried out. It seems, however, that the increase in resistance corresponds to a transition from amorphous to crystalline Na_2S_3. Such a transition could also be observed microscopically.

4. Discussion

The behaviour of the e.m.f. during thermal cycling

(Fig. 3) can be understood by looking at the phase diagram (Fig. 1). During freezing, for all Na_2S_x compositions with $x \leqslant 4$ the e.m.f. assumes the same value which corresponds to Na_2S_3. This means that the undercooled melt during the very fast solidification changes its composition as it would have done when no undercooling had taken place. In the latter case, when reaching the liquidus line, solid Na_2S_4 would be precipitated, changing the composition accordingly, until at the eutectic the solidus line is reached. As the e.m.f. shows, this process obviously does not take place. Because of the undercooling the composition change occurs in a rather short time. This causes the stepwise decrease in the e.m.f. For $x \geqslant 4$ the melt composition changes the other way, thus reaching the Na_2S_5-eutectic with a stepwise increase of the e.m.f. As Fig. 3 shows, during heating (melting) there are no steps in the e.m.f., but a continuous change. This means that when the solidus line is reached the melt changes composition by following the liquidus line until the entire Na_2S_x is molten. Therefore, as shown by the e.m.f., polysulphides in the frozen state exist only in two-phase compositions. The existance range of Na_2S_4 obviously is so small that it can never be obtained as a single phase. It is interesting to note that the e.m.f. sometimes begins to change well below the melting temperature (see Fig. 3) indicating that some sort of amorphous or glass-like sulphide was formed.

The steps in the resistance (Figs. 4 and 5) correspond to those in the e.m.f. However, during heating there is a distinct step shortly before reaching the liquidus line, which is not the case with the e.m.f. Thus, the particles which melt last contribute the greatest part to the overall cell conductivity. In the solid state a different specific resistance for Na_2S_4 and Na_2S_3 was observed, the difference being more pronounced in the glass tube experiments. The reason for this may be the different kind of mechanical contact. Whereas in the glass tubes the solid Na_2S_x shrinks onto the electrodes, thus providing good contact, in a Na–S cell the solid Na_2S_x may loose contact with the casing (serving as an electrode) because of the large thermal expansion coefficient of Na_2S_x. The graphite fibres obviously play no part in the frozen state, because the absolute value and the activation energy of the resistance is almost the same in cells and in pure Na_2S_x without graphite fibres (Fig. 5). Therefore, no graphite fibres will be in contact with the casing when a Na–S cell is cooled down. The quantitative comparison of the values of the Na–S cell and the polysulphide glass tubes (taking into account the geometric factor of the cell of about 350 cm^2 cm^{-1}) shows good agreement in the case of Na_2S_4, but in the case of Na_2S_3 the values for the Na–S cell lie considerably higher than that for the Na_2S_3 glass tubes. This means that part of the Na_2S_3 looses contact with the Na–S cell casing which is not the case with Na_2S_4. Therefore, with deep discharged cells problems may arise concerning a possible separation of a coating from the inner casing wall.

As shown in Fig. 6, the impedance characteristic at low frequencies is a straight line with a slope of about 45°. This suggests that the processes involved are diffusion limited [9]. For a further confirmation the imaginary part of the resistance was plotted against the square root of frequency. Fig. 7 shows that the results were straight lines at high temperatures, whereas at temperatures around the freezing temperature the lines at higher temperatures became curved. From the slope of the straight lines at higher temperatures the diffusion constant can be calculated, provided the concentrations of the active species are known [9]. The diffusion impedance is:

$$R_\mathrm{d} = \frac{RT}{n^2F^2}\,\frac{1}{\omega^{1/2}}\sum\frac{\nu_\mathrm{i}^2}{\bar{c}_\mathrm{i}\,(D_\mathrm{i})^{1/2}} \qquad (1)$$

where ω is the angular frequency, ν_i the stoichio-

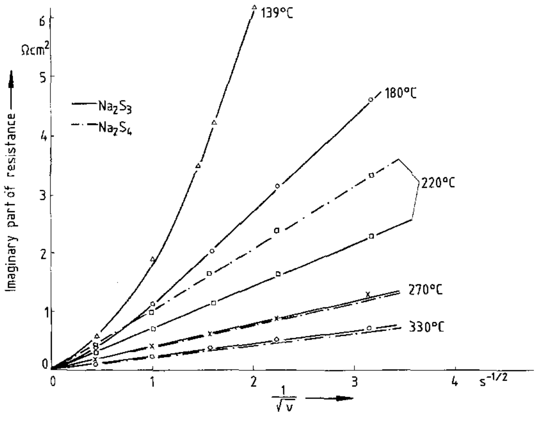

Fig. 7. Imaginary part of the impedance of Na_2S_3 and Na_2S_4 in glass tubes (without graphite felt) versus the reciprocal square root of frequency for different temperatures.

metric factor, c_i the concentration and D_i the diffusion constant of the substances participating in the diffusion. However, because the data given in the literature [10–12] regarding the concentration c_i vary considerably, no attempt was made at this time to calculate the diffusion constant explicitly. As can be seen from the slope of the lines in Fig. 7, the diffusion constant increases with temperature. There is no difference in the diffusion constant between Na_2S_3 and Na_2S_4 at high temperatures. However, at 220° C, which is shortly above the freezing point of undercooled Na_2S_4 (see Fig. 5), the diffusion constant of Na_2S_4 is smaller than that of Na_2S_3 at the same temperature. Obviously, there is a kind of freezing 'announcement' which is reflected by the change in the diffusion coefficient. Below the freezing temperature the diffusion coefficient is so low that it could not be measured. In contrast the diffusion coefficient of Na_2S_3, which also decreases during cooling, is measurable even until about 20° C below the freezing point. Below this temperature, however, the diffusion coefficient drops sharply, too. This is announced by the considerable curvature of the line at 139° C. These experiments show that there is a kind of transition state between the molten and the solid state. This may be due to the glassy, amorphous nature of some polysulphides as was also pointed out by others [3]. However, it is surprising that this is also happening in complete cells because the graphite fibres could be expected to serve as nuclei for crystallization.

5. Conclusions

The investigations described above yielded valuable data for the understanding of the behaviour of Na–S cells during thermal cycling. Facts were pointed out which may be important for the analysis of failures due to thermal cycling. The following observations are of importance:

(a) The e.m.f. of Na–S cells show a discontinuity at the freezing point. This is due to undercooling of the sodium polysulphides in the positive electrode. Parallel to the e.m.f. change is a sharp drop in the electric conductivity at the molten–solid transition. Therefore, the e.m.f. and the resistance can be taken as indicator for a phase change. The e.m.f. drop does not necessarily mean that the Na–S cell has failed.

(b) The behaviour of Na_2S_3 is different from the other compositions in the positive electrode in a number of ways. Na_2S_3 shows a greater tendency to undercool and to become amorphous than the other compositions. In the solid state Na_2S_3 has a conductivity which is up to two decades higher than Na_2S_4 and Na_2S_3 will separate from the inner wall of the cell casing during thermal cycling. Diffusion in Na_2S_3 at lower temperatures is higher than in Na_2S_4.

(c) At room temperature a resistance increase can be observed for polysulphides over over several 100 h, indicating a slow phase change from an amorphous to a crystalline state. This is accompanied by a volume change [7], which may be responsible for stresses and failures of the β-Al_2O_3 tube.

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